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Session 5

STRUCTURE OF SHEAR BANDS IN BULK METALLIC GLASSES

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Plastic deformation in metallic glasses is highly localized into very thin regions called shear bands. An understanding of the structure and behavior of shear bands is central to understanding the micromechanisms of deformation in amorphous alloys. Adequately characterizing the structure of disordered materials on length scales characteristic of shear bands (10-100 nm) is, however, a formidable challenge. Here, we describe the results of two techniques that we have applied to the study of shear bands in metallic glasses.

In the first technique, we use quantitative high resolution transmission electron microscopy (HRTEM) to image defects in shear bands. We observe a large concentration of void-like defects in the shear bands, approximately one nanometer in size, that are generated as a result of plastic deformation. These defects appear to form when excess free volume in the shear band coalesces into voids once the shear stress is removed. This idea is supported by a thermodynamic argument that shows that such a process would reduce the free energy of the system. We believe that these voids, once formed, play an important role in further plastic deformation, acting as both stress concentrators and reservoirs of excess free volume.

LOCALIZED CORROSION BEHAVIOR OF A ZIRCONIUM-BASED BULK AMORPHOUS ALLOY RELATIVE TO ITS CRYSTALLINE STATE

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Early fatigue tests of bulk amorphous materials (BAMs) have resulted in fatigue strengths lower than anticipated. It is suspected that environmental effects degrade the fatigue life. A first step toward understanding the corrosion-fatigue phenomenon is to compare the corrosion behaviors of an amorphous alloy and its crystalline counterpart. Amorphous samples of BAA-11, Zr-10Al-5Ti-17.9Cu-14.6Ni (at. %), were prepared by an arc melting and drop-casting process. Some of these samples were heat treated to create the completely crystalline state. All samples were then subjected to cyclic anodic polarization tests in a 3.5 % NaCl (wt. %) electrolyte at room temperature. The test results yielded corrosion potentials, pitting potentials, protection potentials, corrosion current densities, and corrosion rates. The modes of corrosion for both the amorphous and crystalline samples were identified microscopically. A large scatter in some corrosion data appeared to be intrinsic to the BAA-11 drop-cast materials. However, BAA-11 was shown to have superior pitting-corrosion resistance relative to its crystalline counterpart. Specifically, the protection potentials were consistently higher than the corrosion potentials for the amorphous samples, but lower than the corrosion potentials for the crystalline samples. These results indicate that, under natural corrosion conditions, localized corrosion will not occur with time for the amorphous material, but will occur for the crystalline material.

PRECISION DIE CASTING OF OPTICAL SC/MU CONVERSION SLEEVE

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It is well known that bulk metallic glasses (BMG) are suitable for near net shaping by die casting and other methods in three dimensional form. In the last several years, we have been developing the precision die casting process of BMG ($Zr_{55}Al_{10}Ni_5Cu_{30}$) and application for the SC/MU conversion sleeve. The features of precision die casting method are high injection speed and high pressure.

The SC/MU conversion sleeve is one of optical parts, which holds two kinds of different size optical connector in diameter. The outer diameter is 3.0mm at SC side and 1.75mm at MU side, respectively. The thickness of the SC/MU conversion sleeve is only 0.25mm.

To decrease optical connection loss, it is necessary to control micron order surface roughness and size accuracy. In addition, good corrosion resistance and good wear resistance are required.

The size accuracy of the SC/MU conversion sleeve produced by precision die casting method is $\pm 1\text{ }\mu\text{m}$, and optical connection loss (Li) is less than 0.3dB of a standard value. Moreover, BMG has good thermal stability. The change of Li is less than 0.2dB even in a heat cycle test of -40 degree to 75 degree. Furthermore, the wear resistance is improved by a surface oxidation treatment in air. The SC/MU conversion sleeve produced by BMG has a superior character for optical parts.

THE AIR-OXIDATION BEHAVIOR OF THE Zr-Cu-Al-Ni AMORPHOUS ALLOY AT 300-425°C

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The oxidation behavior of Zr-Cu-Al-Ni bulk amorphous and crystalline alloys (with the same composition of Zr-30%Cu-10%Al-5%Ni in at.%) was studied over the temperature range 300-425°C in air. In general, the oxidation kinetics of both amorphous and crystalline alloys followed the two-stage parabolic rate law at $T \geq 350^\circ\text{C}$, while the 300°C-datum of the amorphous alloy oxidized near the linear behavior. The oxidation rate constants of the amorphous alloy are slightly higher than those of the crystalline alloy.

The scales formed on the amorphous alloy consisted of mostly tetragonal-ZrO₂ at 300°C, while monoclinic- and tetragonal-ZrO₂ and some CuO were detected at higher temperatures. The scales formed on the crystalline alloy consisted of mostly Al₂O₃, some tetragonal-ZrO₂ and very weak monoclinic-ZrO₂ at 300°C, while the scales formed on higher temperatures consisted of mostly monoclinic-ZrO₂, some CuO and Cu₂O, and weak tetragonal-ZrO₂. It is possible that the formation of Al₂O₃ (at 300°C) and CuO/Cu₂O (at $T \geq 350^\circ\text{C}$) of the crystalline alloy is responsible for the reduction of the oxidation rates compared with those of amorphous alloy.

MECHANICAL ALLOYED Ti-Cu-Ni-Si-B AMORPHOUS ALLOYS WITH SIGNIFICANT SUPERCOOLED LIQUID REGION

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Exploring amorphous alloys with a large supercooled liquid region before crystallization is of great importance because the appearance of the large supercooled liquid region is expected to cause the production of a bulk amorphous alloy. The large supercooled liquid region with a temperature interval above 60K had been observed in amorphous Zr-, La, and Mg-based alloys. However, a survey of the available literature indicates that little work has been performed on the formation of Ti-based amorphous alloy with large supercooled liquid region. Ti is lighter and cheaper element as compared with Zr, and Ti-based amorphous alloys are expected to have better properties than that of Zr-based amorphous alloys. In this study, we have investigated the possibility of preparing amorphous Ti-Cu-Ni-Si-B powders by mechanical alloying of crystalline elemental powder mixtures using a shaker ball mill. The glass-forming ability and the T_g and T_x characteristics of a large group of Ti-Cu-Ni-Si-B alloys were determined by using X-ray diffraction and differential scanning calorimetry (DSC). The results indicated that several amorphous alloy samples were found to exhibit a wide supercooled liquid region before crystallization. This is believed to be the first evidence for the appearance of a supercooled liquid region for mechanically alloyed Ti-Cu-Ni-Si-B amorphous powders. The finding of the new Ti-Cu-Ni-Si-B amorphous alloys with wide supercooled liquid region is promising the future development of a new bulk amorphous alloy through powder metallurgy route.

CONSOLIDATION OF AMORPHOUS Ni-Zr-Ti-Si POWDERS BY VACUUM HOT-PRESSING METHOD

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The techniques to synthesize amorphous alloys via solid-state amorphization reaction include hydrogenation, multilayer interdiffusion, and mechanical alloying (MA). As previous investigations demonstrated, formation of amorphous powders with wide supercooled liquid region have been successfully prepared in Mg-Y-Cu, Zr-Al-Cu-Ni and Zr-Ti-Al-Cu-Ni systems by mechanical alloying method. The product material of mechanical alloying is in powdered form and is suitable for compaction and densification in many shapes. The consolidation of Mg-Y-Cu and Zr-Al-Cu-Ni amorphous alloy powders has been carried out by warm consolidation of mechanically alloyed powders in the viscous state above T_g . From the importance of Ni-based alloys as engineering materials, it is worth to explore the possible method for preparing bulk Ni-based amorphous alloys. In this study, Ni-Zr-Ti-Si amorphous alloy powder exhibiting a wide supercooled liquid region has been prepared by mechanical alloying of elemental powders. Bulk Ni-Zr-Ti-Si amorphous alloy was produced by consolidating the as-milled powders with a uniaxial vacuum hot press at temperatures inside the supercooled liquid region. For several bulk samples, no data corresponding to a crystalline phase is observed in the DSC curves and X-ray diffraction patterns. Examination of transverse cross sections for these bulk samples by SEM shows a small amount of porosity is apparent in the cross section, indicating that the consolidation parameters are not yet fully optimized. Partial oxidation of the as-milled powders might be responsible for the non-optimum consolidation and the residual porosity.

EFFECTS OF Sc ADDITION ON THE GLASS FORMABILITY OF $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ ALLOY

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In recent years, metallic glasses with thicknesses ranging from 1 mm to several cm have been successfully developed. Selected elements are commonly added to well-known glass-forming alloys such as Zr-Cu, with the aim of depressing the liquidus temperatures and increasing the temperature range (or so-called supercooled liquid region), between the temperatures of glass transition, T_g , and of crystallization, T_x . The present study has used press forging and die casting process to vitrify ZrCu-based alloys. It was difficult to obtain a complete amorphous structure using the water-cooled copper mold casting process due to its insufficient cooling rate. However, we have found a beneficial effect of small addition of Sc on the glass formability of Zr-based alloy, by exhibiting a high glass forming ability (GFA). A $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ amorphous plate with a size of 3mm x 50mm x 70mm was thus obtained by the copper mold casting method. The amorphous structure of alloy was confirmed by X-ray diffractometry and differential scanning calorimetry. The $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ amorphous alloy revealed many important characteristics for bulk metallic glasses, such as a large supercooled liquid region of $\sim 77\text{K}$ before crystallization, a reduced glassy temperature (T_g/T_l) of 0.61 and a relatively high microhardness value of 504 Hv. In this paper, effects of Sc addition on the glass formability of alloy will be presented and discussed in light of the microstructure/property results obtained.

MECHANICAL PROPERTIES OF TUNGSTEN FIBER REINFORCED

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Tungsten fiber reinforced $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ metallic glass composites were fabricated and characterized. The mechanical properties under compression and tension experiments were investigated for the composites. Tungsten reinforcement greatly increased compressive strain to failure compared to the unreinforced $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ metallic glass. The compressive failure mode changed from a single shear band to multiple shear bands and to localized fiber bucking and tilting as W volume fraction increases. Tensile toughness changed to some extent due to different interface reactions, the composites with weakly bonded W fibers, provided the largest increase in tensile strain to failure. The reason for the increased mechanical properties is discussed.

A ROLE OF GLASS FORMING COMPOUNDS IN DESIGN OF FERROUS BASED BULK METALLIC GLASSES

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It is known that bulk metallic glass (BMG) forming Zr-alloys with extremely high glass forming ability (GFA) are based on original eutectics. These eutectics are formed by two- or three- component glass forming compounds (GFCs) and at least one of them is Laves phase. Recently, bulk amorphous $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$; $Zr_{57}Cu_{20}Ni_8Al_{10}Ti_5$ samples were produced successfully starting from known GFC using mechanical alloying (MA) followed by consolidation of powder in Tg-Tx range. The same approach was developed in this work for design of ferrous BMGs. We have used an idea that chemical composition of any BMG forming alloy might be obtained as a mixing of some 'virtual' GFCs. For example, two GFCs: Fe_3B and hypothetical multicomponent Laves phase were supposed to produce known $Fe_{61}Co_7Zr_{10}Mo_5W_2B_{15}$ BMG. In fact, amorphous phase has been formed both in 1-4 mm rods quenched from melt and in mechanically alloyed powders starting from the supposed GFCs taken at calculated ratio. It should be also noted that 1) on diffraction data multicomponent Laves phase (Fe_2Zr type) was prepared by arc melting as single phase solid solution and 2) melting point of MA powder was appeared the same as for molten alloy.